

USE OF SELECTED ADVANCED OXIDATION PROCESSES (AOPs) FOR WASTEWATER TREATMENT – A MINI REVIEW

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ABSTRACT

Advanced oxidation processes (AOPs) are widely used for the removal of recalcitrant organic constituents from industrial and municipal wastewater. The aim of this study was to review the use of titanium dioxide/UV light process, hydrogen peroxide/UV light process and Fenton's reactions in wastewater treatment. The main reactions and the operating parameters (initial concentration of the target compounds, amount of oxidation agents and catalysts, nature of the wastewater etc) affecting these processes are reported, while several recent applications to wastewater treatment are presented. The advantages and drawbacks of these methods are highlighted, while some of the future challenges (decrease of operational cost, adoption of strategies for processes integration) are discussed.

KEYWORDS: TiO₂/UV; H₂O₂/UV; Fenton; Photo-Fenton; Wastewater.

1. INTRODUCTION

A wide range of organic compounds is detected in industrial and municipal wastewater. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) pose severe problems in biological treatment systems due to their resistance to biodegradation or/and toxic effects on microbial processes. As a result, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of great concern. Among them, advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, surfactants, colouring matters, pharmaceuticals and endocrine disrupting chemicals. Moreover, they have been successfully used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes.

The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (HO•) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and nonselectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions comparing to conventional oxidants such as H₂O₂ or KMnO₄ (Gogate and Pandit, 2004a). Once generated, the hydroxyl radicals can attack organic chemicals by radical addition (Eq. 1), hydrogen abstraction (Eq. 2) and electron transfer (Eq. 3) (SES, 1994). In the following reactions, R is used to describe the reacting organic compound.



A great number of methods are classified under the broad definition of AOPs (Table 1). Most of them use a combination of strong oxidizing agents (e.g. H_2O_2 , O_3) with catalysts (e.g. transition metal ions) and irradiation (e.g. ultraviolet, visible). Among different available AOPs producing hydroxyl radicals, titanium dioxide/UV light process, hydrogen peroxide/UV light process and Fenton's reactions seem to be some of the most popular technologies for wastewater treatment as shown by the large amount of data available in the literature. A search in Scopus database revealed that more than 1000 papers have been published for the applications of these methods in wastewater treatment during the last decade. In the present study, a mini review on the aforementioned processes has been performed. The main reactions and the parameters that affect these processes are discussed, whereas several recent applications are presented.

Table 1. Advanced oxidation processes available in the literature

Hydrogen peroxide/UV light	Ozone/Titanium dioxide
Hydrogen peroxide/ozone	Fenton's reactions (Fe^{2+}/H_2O_2 , $H_2O_2/Fe^{2+}/UV$)
Titanium dioxide/UV	Sonolysis
Ozone/UV	Ozone sonolysis
Ozone/UV/Hydrogen peroxide	Catalytic oxidation
Ozone/Titanium dioxide/Hydrogen peroxide	Supercritical water oxidation

2. USE OF AOPs IN WASTEWATER TREATMENT

2.1 Titanium dioxide/UV light process

In TiO_2 /UV light process, a titanium peroxide semiconductor absorbs UV light and generates hydroxyl radicals. Specifically, during UV illumination of TiO_2 , conduction band electrons and valence band holes are initially yielded (Eq. 4). Band electrons interact with surface adsorbed molecular oxygen to yield superoxide radical anions (Eq. 5), while band holes interact with water to produce hydroxyl radical (Eq. 6) (Crittenden *et al.*, 2005):



Organic compounds can undergo oxidative degradation through their reactions with valence bond holes, hydroxyl and peroxide radicals as well as reductive cleavage through their reactions with electrons.

So far, TiO_2 /UV light process has been extensively used for wastewater treatment. The key advantages of this process are the operation at ambient conditions, the lack of mass transfer limitations when nanoparticles are used as photocatalysts and the possible use of solar irradiation. Moreover, TiO_2 is a cheap, readily available material and the photogenerated holes are highly oxidizing. In addition, TiO_2 is capable for oxidation of a wide range of organic compounds into harmless compounds such as CO_2 and H_2O (Chatterjee and Dasgupta, 2005).

The major factors affecting TiO_2 /UV light process are: initial organic load, amount of catalyst, reactor's design, UV irradiation time, temperature, solution's pH, light intensity and presence of ionic species. The use of excessive amounts of catalyst may reduce the

amount of energy being transferred into the medium due to the opacity offered by the catalyst particles (Gogate and Pandit, 2004a). Reactor's design should assure that uniform irradiation of the catalyst surface is achieved (Ray, 1999). For temperature values between 20 and 80 °C, a minor effect of temperature has been noticed. However, at temperature higher than 80 °C, a reduction of the reaction rate has been reported (Herrmann, 1999). Solution's pH has a complex effect on photocatalytic oxidation rates. For weakly acidic pollutants, reaction rates increase at lower pH (Andreozzi *et al.*, 2000). On the other hand, pollutants which are hydrolyzed under alkaline conditions may show an increase of reaction rate with increase of pH (Choi and Hoffmann, 1997). Finally, the presence of ionic species could affect the degradation process via adsorption of the pollutants, absorption of UV light and reaction with hydroxyl radicals (Gogate and Pandit, 2004a).

Several recent applications of TiO₂/UV light process in wastewater treatment are presented below. Photocatalytic oxidation has been extensively used to treat olive-oil mill wastewater (Marques *et al.*, 1996; Vigo and Cagliari, 1999). In a recent study, TiO₂ under UV irradiation was used for the treatment of diluted (1/100) olive mill wastewater. After 24 h and in the presence of 1 g l⁻¹ TiO₂, almost 22% and 94% of COD and phenols was removed (El Hajjouji *et al.* 2008). Chatzisyneon *et al.* (2008) investigated the use of this process for treatment of olive processing wastewater. According to the results, treatment efficiency was increased with decreasing initial COD and increasing contact time and catalyst concentration. The use of this process as a pretreatment method resulted in reduced biodegradability of treated wastewater comparing to the influents. This observation indicated that most of the biodegradable compounds initially present in wastewater were destroyed or/and less biodegradable intermediates were formed.

Photocatalysis with titanium dioxide was used in order to investigate the oxidation of phenol containing in wastewater and to study the effects of initial phenol concentration, amount of catalyst, solution's pH and light intensity (Laoufi *et al.*, 2008). Almost 99% of the target compound was removed after 4 hours of irradiation. Increase of light intensity from 15 W to 400 W and increase of the amount of TiO₂ from 0.1 to 1 g l⁻¹ enhanced phenol degradation.

The photocatalytic degradation of Direct Red 23 (azoreactive textile dye) was investigated in UV/TiO₂ system (Sohrabi and Ghavani, 2008). The effect of pH and catalyst loading on the reaction rate was ascertained and optimum conditions for maximum degradation were determined. According to the results, acidic pH was proper for the photocatalytic removal of Direct Red 23. The dye decomposition rate increased with concentration of TiO₂ up to 4 g l⁻¹, and then decreased with increasing TiO₂ concentration. At lower loading levels, photonic adsorption controls the reaction extent due to the limited catalyst surface area. Light scattering by catalyst particles predominates over photonic adsorption at higher loading levels.

The concentrate produced from the reverse osmosis treatment of an MBR effluent was treated using photocatalysis (Dialynas *et al.*, 2008). Almost 30% DOC removal was observed in the presence of 0.5 and 1 g l⁻¹ TiO₂ within 50–60 min (dark experiments). When the suspension was irradiated with UV-A light, oxidation of the DOC took place yielding 49 and 41% DOC removal at the high and low catalyst level, respectively.

TiO₂-assisted photocatalytic degradation of pollutants using solar light has been successfully used being an economically viable process that can replace artificial light sources which are costly and hazardous (Muruganandham and Swaminathan, 2004). Usually, solar photocatalytic degradation reactions are carried out by using solar illumination directly (Gonçalves *et al.*, 2005) or using parabolic collectors (Malato *et al.*, 2002). In a recent study, the heterogeneous TiO₂ assisted photocatalytic degradation of wastewater from a thermoelectric power station was studied (Monteagudo *et al.*, 2008). The initial concentration of major pollutants in this type of wastewater was CN⁻ = 10 mg l⁻¹, NH₃ = 150 mg l⁻¹, COD = 1240 mg l⁻¹, TOC = 980 mg l⁻¹ and pH 9.5. The efficiency of

photocatalytic degradation was determined from the analysis of cyanide and formate removal. Cyanide and formate degradation under solar irradiation in the presence of TiO₂ alone was not effective since no oxidizing agent is present and generation of HO• radicals were negligible. The simultaneous use of H₂O₂ (solar/H₂O₂/TiO₂ system) enhanced degradation of wastewater containing cyanides and formates. As a result, under the optimum conditions (pH = 6, temperature = 40 °C, H₂O₂ = 6.5 g l⁻¹, TiO₂ = 1.5 g l⁻¹), the treated wastewater showed the following results after 180 min: CN⁻ = 0 mg l⁻¹, NH₃ = 22 mg l⁻¹, COD = 50 mg l⁻¹, TOC = 14 mg l⁻¹.

In another study, photodegradation aided by a catalyst (TiO₂) was studied for removing EDCs (estrone, 17β-estradiol) using sunlight and UV irradiation (Zhang and Zhou, 2008). More efficient degradation was observed with UV irradiation (253 nm), with the rate constants being increased to 2.7 and 2.5 h⁻¹ for the two compounds. Under natural sunlight, the degradation of estrone and 17β-estradiol followed a pseudo-first-order kinetics, with a rate constant of 0.01 h⁻¹.

Unfortunately, in TiO₂/UV light process most of the produced holes and conduction band electrons (Eq. 4) recombine before they undergo any chemical reactions. To avoid this phenomenon, doping metal ions into the TiO₂ lattice has been used (Sahoo *et al.*, 2005a; b). In a recent study, Behnajady *et al.* (2008) reported that silver doped TiO₂ was more efficient than undoped TiO₂ at photocatalytic degradation of C.I. Acid Red 88. This positive effect of silver on dye degradation was explained by its ability to trap electrons.

2.2 Hydrogen peroxide/UV light process

This process includes H₂O₂ injection and mixing followed by a reactor that is equipped with UV light (200 to 280 nm). During this process, ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. The reactions describing UV/H₂O₂ process are presented below (Buxton *et al.*, 1988):



In the aforementioned equations, Eq. 7 is the rate limiting reaction because the rates of the other reactions are much higher than that of Eq. 7. Theoretically in UV/H₂O₂ process, the higher initial hydrogen peroxide concentration produces higher hydroxyl radical concentration (Eq. 7), which decomposes more target compound. However, an optimal hydrogen peroxide concentration exists because overdosing of hydrogen peroxide would lead to reaction with hydroxyl radical and formation of HO₂• (Eq. 8).

UV/H₂O₂ process is efficient in mineralizing organic pollutants. A disadvantage of this process is that it cannot utilize solar light as the source of UV light due to the fact that the required UV energy for the photolysis of the oxidizer is not available in the solar spectrum (Niaounakis and Halvadakis, 2006). Moreover, H₂O₂ has poor UV absorption characteristics and if the water matrix absorbs a lot of UV light energy, then most of the light input to the reactor will be wasted. Finally, special reactors designed for UV illumination are required, while residual H₂O₂ should be addressed (Crittenden *et al.*, 2005).

The major factors affecting this process are the initial concentration of the target compound, the amount of H₂O₂ used, wastewater pH, presence of bicarbonate and

reaction time. Specifically, the kinetic rate constant for the degradation process is inversely proportional to the initial concentration of the pollutant. As a result, wastewater dilution should be done at an optimum level (Gogate and Pandit, 2004b). Moreover, there is an optimum concentration for H₂O₂. Beyond this limit, the presence of H₂O₂ is detrimental to the degradation reaction due to scavenging action. Lower pH values (2.5-3.5) are usually preferred, however pH values are dependent on the pKa of the target compounds.

UV/H₂O₂ process has been widely used for dyes removal. In a recent study investigating C.I Acid Orange 7 (a commonly detected dye in textile wastewater) removal, Daneshvar *et al.* (2008) reported that the absence of UV radiation or H₂O₂ decreased dye removal efficiency to almost zero. Increase of H₂O₂ concentration up to 2 mmol l⁻¹ and increase of pH at basic values enhanced dye removal efficiency, while the increase of bicarbonate anion concentration affected negatively its removal. Rezaee *et al.* (2008) used this process for decolorization of Reactive blue 19 and the effects of operating parameters such as H₂O₂ dosage, initial dye concentration, pH and UV dosage, on decolorization were evaluated. According to the results, the dye solution was completely decolorized under optimal H₂O₂ dosage (2.5 mmol l⁻¹) and low-pressure mercury UV-C lamps (55 w) in less than 30 min. The decolorization rate increased linearly with UV dosage and nonlinearly with increasing initial H₂O₂ concentration.

The combined use of UV/H₂O₂ with ultrasonic waves (US) has also been reported in order to enhance color removal during dyeing wastewater treatment (Fung *et al.*, 1999; 2001). In a recent study, the efficiency of UV/H₂O₂ and US/UV/H₂O₂ processes on the removal of malachite green as a model contaminant from textile industry was investigated (Behnajady *et al.*, 2008). According to the results, US/UV/H₂O₂ was the most effective process for the degradation of malachite green as the use of ultrasound contributed together with photolysis to the scission of H₂O₂. The removal rate of malachite green followed first-order kinetics, whereas the reaction rate increased with increasing temperature (294 to 307 K), power density (0.049 to 1.163 W ml⁻¹) and decreasing initial concentration of the target compound (10 to 2 mg l⁻¹).

UV/H₂O₂ process has been used for the degradation of phenolic compounds that are detected in olive mill wastewater (Benitez *et al.*, 1996; 1998). In a recent study, Ugurly and Kula (2007) investigated the effect of hydrogen peroxide dosage, pH, UV and natural sunlight on the decolourization and removal of organic carbon and phenols from olive mill wastewater. In samples exposed to natural sunlight, almost 90% removal was achieved (H₂O₂/wastewater = 3 ml/100 ml). For the aforementioned experimental conditions, the use of lime enhanced phenol and lignin removal, reaching to almost 100% and 40%, respectively. Finally, use of the aforementioned process for COD removal from oil recovery industry wastewater showed that almost 90% of the COD could be removed (initial COD concentration = 1050 mg l⁻¹, COD/H₂O₂ = 1/2, pH = 3, temperature = 39-43 °C) (Dincer *et al.*, 2008). Increase of initial COD concentration resulted to a decrease of the process performance.

2.3 Fenton's reactions

Fenton's reagent, a mixture of ferrous iron (catalyst) and hydrogen peroxide (oxidizing agent), has been known as a powerful oxidant for organic contaminants. The mechanism of the Fenton process is reported below (Neyens and Baeyens, 2003; Niaounakis and Halvadakis, 2006):



The photo Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) involves the $\text{HO}\cdot$ formation through photolysis of hydrogen peroxide ($\text{H}_2\text{O}_2/\text{UV}$) and Fenton reaction ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$). In the presence of UV irradiation, the ferric ions (Fe^{3+}) produced in Equation 13 are photocatalytically converted to ferrous ions (Fe^{2+}), with formation of an additional equivalent of hydroxyl radical (Eq. 17) (Moraes *et al.*, 2004).



Similarly to Equation 15, the hydroxyl radicals formed react with organic species, promoting their oxidation. Based on the fact that Fenton reaction is accelerated by light, photo Fenton reaction gives faster rates and higher degrees of mineralization comparing to conventional Fenton process (Pignatello *et al.*, 2006). Due to the fact that this reaction can be driven by low energy photons, it can also be achieved using solar irradiation (Torrades *et al.*, 2004). This fact can significantly reduce the operational cost of the treatment.

The major parameters affecting Fenton process are solution's pH, amount of ferrous ions, concentration of H_2O_2 , initial concentration of the pollutant and presence of other ions (Gogate and Pandit, 2004a). The optimum pH for Fenton's reagent processes ranges from 2 to 4. At pH higher than 4, the Fe^{2+} ions are unstable and they are easily transformed to Fe^{3+} ions, forming complexes with hydroxyl. Moreover, under alkaline conditions H_2O_2 loses its oxidative power due to its breakdown to oxygen and water (Niaounakis and Halvadakis, 2006). Due to the above, wastewater pH adjustment is usually needed before treatment with Fenton processes. Increase of ferrous ions and H_2O_2 concentration results to an increase of degradation rate (Lin and Lo, 1997). However, having in mind the toxicity of H_2O_2 to several microorganisms, the use of excess amounts of H_2O_2 could possibly deteriorate overall degradation efficiency for cases that Fenton process is followed by biological oxidation (Gogate and Pandit, 2004a). Fenton oxidation of organic compounds is inhibited by phosphate, sulfate, fluoride, bromide and chloride ions. Inhibition by these species may be due to precipitation of iron, scavenging of $\text{HO}\cdot$ or coordination to dissolved Fe(III) to form a less reactive complex (Pignatello *et al.*, 2006).

Electro-Fenton methods include electrochemical reactions for the in situ generation of the reagents used for the Fenton reaction. The generated reagents depend on solution conditions, cell potential and nature of electrodes (Pignatello *et al.*, 2005). Ferrous ions may be produced by oxidative dissolution of anodes such as iron metal (Arienzo *et al.*, 2001) or by reduction of ferric ions at an inert cathode such as platinum (Qiang *et al.*, 2003). Moreover, H_2O_2 may be produced by dioxygen reduction at the cathode (Casado *et al.*, 2005). Beside the advantages originating from the in situ generation of the reagents, Electro-Fenton methods still face several obstacles concerning the production of H_2O_2 , the gradual corrosion of electrodes and the produced sludge treatment (Pignatello *et al.*, 2005).

Despite the drawbacks that Fenton processes present (e.g., requirement for acidic conditions, interference by substances that complex iron ions, production of iron oxide sludge), so far, Fenton and photo Fenton processes have been used for the treatment of several types of wastewater including those produced in dye manufacture, pulp bleaching, agricultural processing and chemical manufacture. Moreover, biological wastewater treatment may be improved with the addition of a Fenton pretreatment step.

In a recent study investigating COD removal from oil recovery industry wastewater using Fenton process, Dincer *et al.* (2008) reported that 86% reduction of COD was achieved for H_2O_2 to Fe^{2+} mass ratio equal to 8.7 (w/w) (initial COD = 21000 mg l^{-1} , reaction time = 60 min, pH = 3). When photo Fenton process was used for the treatment of diluted wastewater, COD removal equal to 81% was achieved (initial COD = 4200 mg l^{-1} ,

reaction time = 210 min, $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 168$ w/w, pH = 3). According to Moraes *et al.* (2005) photo-Fenton process is sufficient for the removal of hydrocarbons from saline wastewater. The initial concentration of ferric ion (Fe^{2+}) and salinity had a significant influence on the degradation process, while the impact of hydrogen peroxide concentration was minor. Photodegradation of hydrocarbons was higher than 81% in all experimental conditions used ($\text{H}_2\text{O}_2 = 100\text{-}200$ mM, $\text{Fe}^{2+} = 0.5\text{-}1$ mM, $\text{NaCl} = 200\text{-}2000$ mg l^{-1} , reaction time = 4.5 h). Moreover, photo-Fenton process combining with aerobic biological processes have been successfully used for the treatment of saline industrial wastewater containing almost 0.6 g l^{-1} α -methylphenylglycine (Malato *et al.*, 2007).

Use of photo-Fenton reaction for the treatment of olive mill wastewater (OMWW) resulted to a color removal higher than 90% (Ferreira *et al.*, 2008). In that study, the optimal conditions were observed when 6 ml of H_2O_2 (70%) and 1 ml of FeSO_4 (0.5 M) were added to 50 ml of OMWW (reaction time = 6 days, pH = 4.2). In another study, El Gohary *et al.* (2008) investigated the use of Fenton process for the pretreatment of OMWW. COD removal up to 83% was achieved, at pH values ranging from 2 to 3 (initial COD = 23400 mg l^{-1} , reaction time = 90 min, $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 10$).

Mosteo *et al.* (2008) used heterogeneous photo Fenton process for the pretreatment of winery wastewater. Almost 50% decrease of TOC was observed when an initial H_2O_2 concentration of 0.1 M was used, over 24 hours treatment. Finally, Fenton's oxidation has been applied for the pretreatment of landfill leachate. Petruzzelli *et al.* (2007) reported that under optimal conditions (initial COD = 10915 mg l^{-1} , reaction time = 120 min, $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 13$ w/w, pH = 3.2) almost 50% COD removal was observed.

3. CONCLUSIONS AND FUTURE PERSPECTIVES

The great interest of the academic community for the use of AOPs in wastewater treatment is reflected by the significant number of publications that have been produced during the last decade. So far, TiO_2/UV light process, $\text{H}_2\text{O}_2/\text{UV}$ light process and Fenton's reactions have been extensively used for the removal of COD, TOC, dyes, phenolic compounds, endocrine disrupting chemicals and other recalcitrant organic chemicals from industrial and municipal wastewater. The major factors affecting these processes are the initial concentration of the target compounds, the amount of oxidation agents and catalysts, the light intensity, the irradiation time and the nature of the wastewater's solution (pH, presence of solids and other ions). The role of the aforementioned parameters on AOPs performance has been sufficiently described for different types of wastewater.

However, several topics such as the relatively high operational cost of these processes due to the use of costly chemicals and the increased energy consumption, as well as the formation of unknown intermediates which in some cases could be more toxic than the parent compounds remain unsolved. Moreover, all these methods are susceptible to scavenging of hydroxyl radicals by non target substances, while they are not suitable for certain categories of toxic compounds which resist attack by hydroxyl radicals.

Based on the above, the main future challenges for using AOPs in wastewater treatment could be the development of efficient and low cost materials to promote sufficient treatment, the use of renewable energy sources, the adoption of strategies for processes integration, the targeting of new classes of pollutants and the commercialization of processes which have been so far used in the laboratory (Comninellis *et al.*, 2008).

For instance, doping TiO_2 with non-metallic elements such as sulphur, nitrogen, carbon could be adopted in order to extend the absorbance wavelength range of TiO_2 and enhance photocatalytic activity (Thompson *et al.*, 2006). The simultaneous or the sequential application of different AOPs could also enhance treatment performance. The use of ultrasonic (US) irradiation with TiO_2 photocatalysis could result to an increase of the produced hydroxyl radicals, while the US could accelerate mass transfer of reagents on TiO_2 surface (Berberidou *et al.*, 2007). The application of separation steps such as

coagulation, sedimentation, filtration before the application of AOPs could remove solids that interfere with these processes. Moreover, the use of AOPs, as a pretreatment step which is followed by biological treatment processes, could achieve lower cost and sufficient organic compounds removal. Finally, the satisfactory designing of large scale photocatalytic reactors in order to achieve uniform irradiation of the entire catalyst surface with the same light intensity would allow the commercialization of this process.

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